

Low-temperature resistivity saturation in the Kondo insulator SmB_6 : Indication for another scenario of hopping-type conductivity

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We provide arguments that dynamical changes of energies of impurity states due to valence fluctuations (VFs) result in non-equilibrium energy distribution function of localized charge carriers. Corresponding hopping type of conductivity that does not require a thermal activation can explain unusual metallic-like conduction of SmB_6 and other Kondo insulators experimentally observed at lowest temperatures. A qualitatively similar hopping process is expected in metal-oxide-semiconductor (MOS) structures due to local dynamical changes of voltage potential in the metal (gate) electrode.

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SmB_6 belongs to the class of intermediate valence (or homogeneously mixed valence) semiconductors,¹ which are also known as Kondo insulators or heavy-fermion semiconductors². The ground state of Sm is coherent superposition of the configurations, $4f^6$ and $4f^55d$, with weight factors 0.3 and 0.7, respectively, giving an effective $4f$ valence of 2.7.³ Although this compound has been studied for more than four decades, many fundamental aspects, especially those associated with the origin of the gap and the unusual low-temperature transport properties remain still unclear. A principal problem represents a metallic-like electrical conductivity of SmB_6 at lowest temperatures.

Electrical resistivity measurements of SmB_6 show a large resistivity increase at decreasing temperature below 50 K with a saturation at high residual value ρ_0 at lowest temperatures.^{4,5,6,7,8} Detailed studies of electrical conductivity $\sigma(T)$ show a temperature non-activated (metallic) channel in $\sigma(T)$, which becomes dominating below about 3 K.^{5,6,7,8,9} An explanation of the high value of ρ_0 requires a superunitary scattering^{2,4} with unphysically high concentration of scattering centers (at least 80 per unit cell⁶). However, according to the Mott-Ioffe-Regel viewpoint, the conventional Boltzmann transport theory becomes meaningless when the characteristic mean free path of the itinerant conduction electrons becomes comparable to, or less than, the interatomic spacing.^{10,11,12} Therefore, the high value of the residual resistivity cannot be attributed to metallic conductivity mediated by itinerant electrons. On the other hand, assuming that electron states in the vicinity of the Fermi level are localized, the present theories require a temperature activated conductivity and an insulating ground state, what is, however, in qualitative disagreement with experimental indications^{5,6,7,8,9} mentioned above. The consequence of this disagreement is that the origin of the residual resistivity/conductivity in SmB_6 can not be consistently explained considering the known mechanisms of electrical conductivity in metals or semiconductors.

In this paper we provide arguments that dynamical changes of energies of localized (impurity) states, which have to be present in SmB_6 due to valence fluctuations

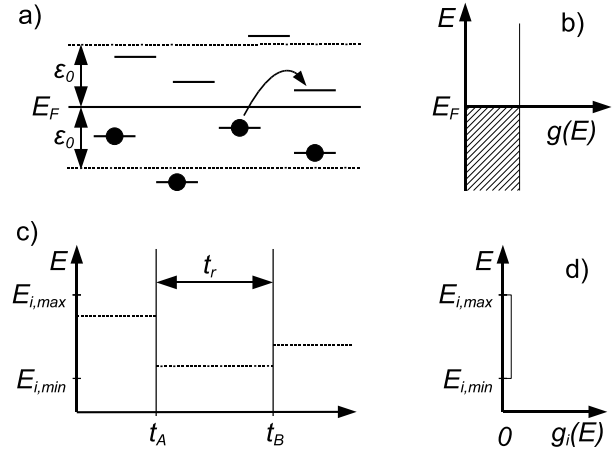


FIG. 1: Schematic depiction of energy of donor levels in the IB of classical semiconductor (a) with corresponding DOS diagram (b), time evolution of the energy of donor impurity due to rearrangements of metallic ions (c) and time-averaged partial DOS (d) corresponding to SIB (see definition in the text).

(VFs), result in a non-equilibrium energy distribution function of localized charge carriers. As a consequence, a temperature nonactivated hopping (tunneling) between localized states occurs yielding metallic-like conductivity at lowest temperatures. We also advert to the fact that qualitatively analogous mechanism should be present in MOS based devices, e.g. in MOS field effect transistors (MOSFETs) because of local dynamical changes of voltage potential in the gate (metal electrode).

Let us start considering a classic semiconductor with a donor impurity band (IB) located in the forbidden gap. Let the Fermi energy, E_F , lies in the IB and the states near E_F are localized, characterized by a constant density-of-states (DOS) function, $g(E)$. In addition, let us suppose that the crystal lattice of the semiconductor contains metal ions Me in two different valence states at least, say Me^{2+} and Me^{3+} , randomly distributed over the lattice. The energy level diagram and the DOS of

the system in a “static” case, when the metal ions do not change their valence, is schematically depicted in Fig. 1a and Fig. 1b, respectively. The electrical conductivity at lowest temperatures in such a system is of a variable-range hopping type^{12,13}, arising from the phonon assisted hopping in a so-called optimal band. The optimal band is a narrow energy interval of the width $2\epsilon_0$ ¹³ centered at the Fermi level with concentration of impurities $N(\epsilon_0) = 2\epsilon_0 g(E_F)$.¹³ Several derivations consistently show that ϵ_0 , being in fact a typical activation energy of a hop, decreases with temperature as $T^{3/4}$, causing a consequent decrease of the impurity concentration in the optimal band. As a result, an average distance between the hopping centers increases as $T^{-1/4}$, and the conductivity follows Mott’s law^{12,13,14}, $\sigma \propto e^{(-T_0/T)^{1/4}}$.

Now, let us consider such rearrangements of metal-ions valences (with a characteristic time constant, t_r , sufficiently long for well defined energies of impurity states) that do not change neither the number of Me^{2+} and Me^{3+} ions, nor the physical properties of the system. Due to different physical properties of Me^{2+} and Me^{3+} ions (e.g. ionic radius or charge), every such rearrangement causes a change of local parameters influencing the energy of impurity states (e.g. chemical pressure acting on the impurity center or the Coulomb interaction between the impurity center and the metallic ions). Consequently, the energies of individual donor states are changed too, as it is schematically shown in Fig. 1c. Performing all the possible rearrangements as defined above, the energy of a donor level, E_i , satisfies the inequality

$$E_{i,min} \leq E_i \leq E_{i,max}, \quad (1)$$

where $E_{i,min}$ and $E_{i,max}$ define the energy window for the donor level. So that, because of VFs, the energy of impurity state at a site i dynamically changes in the interval of the width

$$\Delta E_i = E_{i,max} - E_{i,min}. \quad (2)$$

For purposes of this paper we denote this interval as a single impurity band (SIB). The probability of finding an impurity state i at the energy E from its SIB is characterized by partial-DOS function $g_i(E)$ coupled with $g(E)$ by

$$g(E) = \sum g_i(E), \quad (3)$$

where the summation is performed over all impurity states. Such as E_F lies in the IB, there have to exist also SIBs satisfying the condition

$$E_{i,min} < E_F < E_{i,max}. \quad (4)$$

For these states there is a non-zero probability that some occupied donor levels from the region below E_F shift due to the valence rearrangements to the region above E_F . Analogously, empty donor levels from the region above E_F can shift under E_F . Such energy changes represent

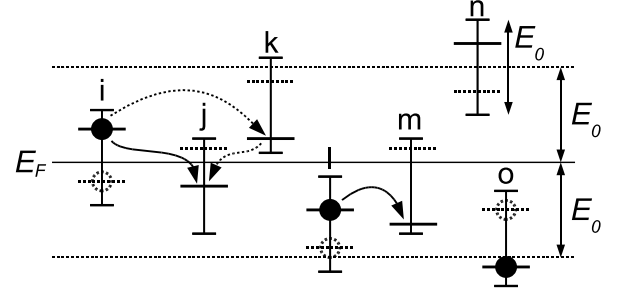


FIG. 2: Schematic depiction of hoppings due to a rearrangement within impurity subnetwork given by inequality (4). The states before rearrangement are represented by dotted symbols, the width of SIBs is shown as “error bars”. The hopping from occupied state i shifted above E_F is to state j directly, or via state k , which is temporarily included in the subnetwork. Hopping to the empty state m which decreased below E_F from occupied state l is another example of possible hopping to the state with less energy.

in fact non-equilibrium excitations driven by the rearrangement process (RP). Therefore, they have to be consequently brought into the equilibrium state, namely via electron hops from occupied states above E_F to empty states with less energy, or via hops to empty states below E_F from occupied states with higher energy. For simplicity let us assume that all SIBs are characterized by an equal width $\Delta E_i \approx E_0$. In such case energies E_i from the SIBs satisfying the inequality (4) lie in the band given by

$$E_F - E_0 < E_i < E_F + E_0. \quad (5)$$

The corresponding donor states, as well as those only temporarily satisfying the inequality (5), form a subnetwork, in which conditions for hops from occupied states to empty states with less energy are intrinsically created, as schematically shown in Fig. 2. Because such hopping processes do not require activation energy, we denote the interval defined by eq. (5) as zero-activation-energy band (ZAEB). The number of states in ZAEB is

$$N(E_0) = 2E_0 g(E_F). \quad (6)$$

Although Eq.(6) has formally the same form as the above mentioned equation for the concentration of hopping centers in the optimal band, considered in the variable-range hopping conductivity¹³, there is a fundamental difference: while the width of the optimal band ($2\epsilon_0$) decreases with temperature as $T^{3/4}$ yielding the *zero* concentration of hopping centers for $T \rightarrow 0$ K, the concentration of hopping centers in ZAEB is always *non-zero* because of a *non-zero* value of E_0 . In fact, this leads to a qualitative conclusion that the hopping process in ZAEB results in a *non-zero* conductivity also for $T \rightarrow 0$ K. Such conclusion can be supported by the following additional arguments.

According to Ambegaokar, Halperin and Langer,¹⁴ the intrinsic transition rate γ_{ij} for an electron hopping from a site i with energy E_i to an empty site j with energy

E_j (in the simplest case, when kT is small compared to $|E_j - E_i|$, and $|E_j - E_i|$ is of the order of the Debye energy or smaller) is well approximated by the “quantum-limit” hopping formula¹⁴

$$\gamma_{ij} = \gamma_0 e^{-2\alpha R_{ij} - (E_j - E_i)/kT} \quad \text{for } E_j > E_i \quad (7)$$

$$\gamma_{ij} = \gamma_0 e^{-2\alpha R_{ij}} \quad \text{for } E_j < E_i, \quad (8)$$

where γ_0 is a constant as defined elsewhere¹⁴ and R_{ij} is the distance between the centers i and j . To estimate the time averaged hopping probability between the centers i and j , we consider a bidirectional hopping process ($i \rightarrow j \rightarrow i \rightarrow \dots$). In a classic semiconductor such a process always requires thermal activation - because of hops to empty states with higher energy, represented by Eq. (7). The situation is qualitatively different in the semiconductor, where RPs take place. If we introduce a parameter ν_{ij} denoting the probability that due to the RP (not due to phonon absorption) an occupied state i occurs at higher energy level than an empty state j (i.e. $E_j > E_i$ before RP, and $E_j < E_i$ after RP), then the probability of the hopping from site i to site j will be $\nu_{ij}\gamma_0 e^{-2\alpha R_{ij}}$. In the case that the ratio

$$\beta_{ij} = \frac{\nu_{ij}\gamma_0 e^{-2\alpha R_{ij}}}{\gamma_0 e^{-2\alpha R_{ij} - (E_j - E_i)/kT}} = \frac{\nu_{ij}}{e^{-(E_j - E_i)/kT}} \quad (9)$$

is greater than 1, the predominating hops at a finite temperature T are not longer the phonon assisted ones, but those “driven” by RPs. At sufficiently low temperatures $\beta_{ij} > 1$ for any pair of i and j with nonzero ν_{ij} . So that, the (bidirectional) intrinsic transition rate at lowest temperatures ($\beta_{ij} \gg 1$) can be approximated by

$$\gamma_{ij} \approx \nu_{ij}\gamma_0 e^{-2\alpha R_{ij}} \quad (10)$$

and the probability of electron hops due to dynamical changes of the impurity energy levels, p_h , in an macroscopic system with RPs can be approximately expressed by

$$p_h \propto p_{rp} e^{-2\alpha R^*}. \quad (11)$$

Here p_{rp} is an effective parameter describing the probability of finding a pair consisting of an occupied state and an empty state of less energy at an effective distance R^* . Such hopping probability represents, in fact, the tunneling process across the barrier of “thickness” R^* . Taking into account a finite value of $R^* \sim N(E_0)^{-1/3}$, where $N(E_0)$ is given by Eq. (6), the resulting “tunneling” conductivity in the ZAEB of non-zero width $\sim 2E_0$ has to be non-zero for $T \rightarrow 0$ K. The crossover from the phonon assisted hopping type of conductivity to the conductivity driven by RPs is expected at temperatures corresponding to $\beta \approx 1$, where β is an effective parameter of partial parameters β_{ij} given by Eq. (9).

The above sketched scenario indicates how the hopping process in the IB can be induced by “slow” VFs. For application of this scenario to SmB₆ with fast VFs,

we take into account the following facts. Supposing that Fermi level of SmB₆ lies in the IB of the width W_{IB} and assuming a subnetwork of impurity states that can be considered as ZAEB, the upper estimation for E_0 follows from the inequality $0 < 2E_0 < W_{IB} < E_g$, where E_g is the width of the forbidden gap in SmB₆. Such as experiments give $E_g > 2$ meV, for purposes of our rough estimation we consider E_0 to be less than ~ 1 meV, providing ~ 2 meV for the upper estimation of the energy of non-equilibrium excitations. Based on the Heisenberg relation we estimate the life time of non-equilibrium excitations to be longer than the life time of excitations with energy 2 meV, $t_{exc} = \hbar/2 \text{ meV} \doteq 3.3 \times 10^{-11}$ s. Dynamical changes of the impurity energy levels due to Coulomb interaction between the impurity and the surrounding lattice can be characterized by the time constant of charge fluctuations. The charge fluctuation rate of SmB₆ estimated from phonon spectroscopy studies^{15,16} is between 200 cm^{-1} and 650 cm^{-1} . These values correspond to the characteristic time between 5.1×10^{-14} s and 1.7×10^{-13} s, what are the values more than two order of magnitude less than the life time of non-equilibrium excitations. So that the energy of both, occupied and empty states can vary within their SIBs for many characteristic time constants of charge fluctuations without a change of their occupation. This means that SIBs of occupied and those of empty states overlap in ZAEB (of the width $2E_0$ centered at E_F). Considering that the dynamics of VFs in SmB₆ is temperature independent down to absolute zero, ZAEB persists in the system down to the lowest temperatures. Therefore an energy distribution function (EDF) of charge carriers at the lowest temperatures has to be deviated from the (equilibrium) Fermi-Dirac distribution function (FDDF). As a consequence, electrical conductivity of SmB₆ does not converge to zero at lowest temperatures, such as only the ground state described by FDDF (with all occupied states below E_F and all empty states above E_F at $T = 0$ K) is characterized by zero value of electrical conductivity (of hopping type). Moreover, taking into account the effect of temperature on EDF of charge carriers, the presence of ZAEB of non-zero width $2E_0$ indicates that the charge carrier subsystem is not able to reach temperatures, at which the width of thermal broadening, $\sim kT$, is less than $2E_0$. This implies that the charge carrier subsystem can not be cooled below a certain minimum temperature $T_{min} > 2E_0/k > 0$ K. (Note that such conclusion also opens a question on the relevant definition of the “ground state” in Kondo insulators.) According to our opinion, just a non-equilibrium EDF of charge carriers is a fundamental reason for experimentally observed saturation of electrical conductivity of SmB₆ (and other Kondo insulators, e.g. FeSi)^{17,18,19} at the lowest temperatures.

Based on the discussion above we emphasize that proposed concept of hopping-type conduction is applicable in systems, with energy of localized states driven by *local dynamical* effects. Moreover, if such effects can be induced into the system by external parameters, then

these parameters can be used to control the electrical conductivity of the system. This indicates a possibility to develop new type of active electronic devices. According to our opinion, a relevant example is the influence of local dynamical changes of voltage potential in the gate area of a MOSFET on two-dimensional (2D) conductivity in the device. An energy difference of two (almost identical) localized states in the conducting 2D layer at a mutual distance R^* is governed by voltage difference between the corresponding regions in the gate. Because of non-zero electrical resistance between the regions, thermal noise voltage occurs as follows from Nyquist formula. This causes a fluctuating energy difference between the impurity centers, giving rise to a deviation from the equilibrium FDDF and to a hopping process (driven by gate-noise voltage), in accordance with equation (11). However, in contrast to the above discussed valence-fluctuating semiconductors, it has to be taken into account that the thermal noise voltage vanishes for $T \rightarrow 0$ K. Therefore, if there exists a noise voltage induced metallic-like behavior ($d\rho/dT \geq 0$) dominating at relatively higher temperatures, it has to change to temperature activated transport ($d\rho/dT < 0$) for $T \rightarrow 0$ K, and so $\rho \rightarrow \infty$ for $T \rightarrow 0$ K. Indeed, studies of cooling of 2D electrons in silicon MOSFET reported by Prus and coworkers²⁰ have shown that some of “metallic” $\rho(T)$ curves turn insulating below ~ 300 mK.²⁰

Discussion above adverts to a possible role of local voltage fluctuations in metallic behavior in two dimensions²¹. A detail understanding of this phenomenon seems to be fundamental, as according to the arguments of Abrahams *et al.*²² a noninteracting 2D carrier system with any

amount of disorder has to be localized at zero temperature. More light into the problem should introduce experiments with MOSFET-type devices devoted to *careful* studies of the influence of several types of local dynamical changes of voltage potential in the gate area on (i) the electrical conductivity, on (ii) the noise current, and on (iii) the charge carrier temperature in 2D conducting layer. Especially the latter point is of special importance as it can bring direct experimental proof of the model presented in this paper. It would be also reasonable to verify, whether a novel design of the gate electrode aimed to the *controlled* generation of local (say nano-range) voltage fluctuations or oscillations (for instance due to the current flow in the area of nanostructured gate) can be considered as another, or even alternative, parameter controlling the 2D conductivity in the novel MOSFET-type devices.

In summary, we have provided arguments that dynamical changes of energy of localized states due to valence fluctuations can be the clue for understanding experimentally observed unusual metallic like transport in Kondo insulator SmB_6 and related systems. The proposed hopping scenario also introduces new light into the problem of anomalous metallic-like 2D conductivity and indicates a favorable route for research that can bring experimental verification of the discussed phenomena.

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